

Nucleation Theory and Applications

Edited by
Jörn W. P. Schmelzer



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Preface

Norwegen ist ein großes Land, das Volk ist ungestüm und es ist nicht gut, es mit einem unzureichenden Heer anzugreifen.

Snorri Sturloson, Heimskringla (about 1230)

cited after D.M. Wilson (Ed.):

Die Geschichte der Nordischen Völker,
Orbis-Verlag, München, 2003

The present book consists of contributions, which have been presented and discussed in detail in the course of the research workshops *Nucleation Theory and Applications* organized jointly by scientists from the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research in Dubna, Russia, and the Department of Physics of the University of Rostock, Germany, involving colleagues from Russia, Belorussia, Ukraine, Kazakhstan, Estonia, Bulgaria, Czech Republic, Brazil, United States, and Germany. These workshops have been conducted yearly for about one month in Dubna, Russia, starting in 1997. The intention of these workshops was and is to unite research activities aimed at a proper understanding of both fundamental problems and a variety of applications of the theory of first-order and second-order phase transitions, in particular, and of the typical features of processes of self-organization of matter, in general. The meetings in Dubna have been supplemented hereby by mutual research visits of the participants in the course of the year in order to continue and extend the work performed during the workshops.

By such a combination of the common attempts, the search for solutions to the highly complex problems occurring in this field could be stimulated in a very effective way, and a number of problems could be solved which would otherwise have remained unsolved. The results of these efforts have been published in a variety of journal articles, which will be partly cited in the contributions in the present book. Some of the results have already been reflected in detail in the preceding monograph, *J. Schmelzer, G. Röpke, R. Mahnke (Eds.): Aggregation Phenomena in Complex Systems*, published in 1999 also by Wiley-VCH. It is also planned to continue the series of research workshops in the coming years. Relevant information will be given at the homepage <http://thsun1.jinr.ru> of the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research and can also be requested via electronic mail from the editor of the present book (juern-w.schmelzer@physik.uni-rostock.de).

These workshops could be carried out for such prolonged times only through continued support from a variety of organizations. We would like to mention here in particular, the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) (via Research projects, the TRANSFORM and Heisenberg-Landau programs), the Deutsche Forschungsgemeinschaft (DFG) (via Research projects, travel and conference grants), the Deutscher Akademischer Austauschdienst (DAAD), the Russian Foundation for Basic Research (RFBR), the UNESCO, the BASF-AG Ludwigshafen, the SOROS-Foundation, the State of São Paulo Research Foundation (FAPESP), and the host institution, the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research in Dubna. To all the

above-mentioned organizations and to those not mentioned explicitly, we would like to express our sincere thanks. We would also like to express our gratitude to all the colleagues who helped us in the organization of the workshops.

It also gives us particular pleasure to thank the coworkers of the Vitreous Materials Laboratory (LAMAV) of the Federal University of São Carlos (UFSCar), Brazil, and, especially, the Head of the Department, Professor Edgar D. Zanotto, for their cordial hospitality and the excellent working conditions during the course of the stay of the editor of the present monograph at their laboratory allowing to bring this book to completion.

Rostock, Germany
August 2004

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Dubna, Russia

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São Carlos, Brazil
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1 Introductory Remarks

Jörn W.P. Schmelzer

*If God will send me readers, then, may be,
it will be interesting for them . . .*

Alexander S. Pushkin
cited after: B.S. Cantor: Talks on Minerals
(Astrel, Moscow, 1997) (in Russian)

Clustering processes in first-order phase transformations play an important role in a huge variety of processes in nature, and in scientific and technological applications. An adequate theoretical description of such processes is therefore of considerable interest. One of the tools allowing the theoretical description of such processes is the nucleation theory. The theoretical approach predominantly employed so far in the interpretation of experimental results of nucleation-growth processes is based on the classical nucleation theory, its extensions and modifications. It is supplemented by density functional computations, statistical mechanical model analyses, and computer modeling of model systems allowing us to gain additional insights into the respective processes and to specify the possible limitations of the classical approaches.

Although the basic concepts of the classical approach to the description of nucleation processes were developed about 80 years ago, a number of problems remain, however, unsettled till now which are partly of fundamental character. Several of these problems are analyzed in the present book. One of these analyzes is directed to the method of determination of the coefficients of emission in nucleation theory avoiding the concept of constraint equilibrium distributions (Chap. 3). A second such topic is the proper determination of the work of critical cluster formation for the different processes under investigation. It is discussed in detail in Chaps. 4 (in application to crystallization) and 5 (in application to boiling of binary liquid-gas solutions). A third topic, a relatively recent development of the nucleation theory with a wide spectrum of possible applications, consists in the theoretical description of nucleation and growth processes in solid solutions with sharp concentration gradients (Chap. 10).

The majority of theoretical approaches to the description of nucleation and growth processes rely, as far as thermodynamic aspects are involved, on Gibbs' classical thermodynamic theory of interfacial phenomena. In recent years it has been shown that, by generalizing Gibbs' thermodynamic approach, a number of problems of the classical theory can be resolved. In particular, as is shown in Chap. 11, the generalized Gibbs' approach leads to predictions for the properties of the critical clusters and the work of critical cluster formation, which are equivalent to the results of van der Waals' square gradient and more sophisticated density functional approaches. Some additional new insights, which have been obtained recently employing the generalized Gibbs' approach, are sketched in Chap. 12.

The nucleation theory has the unique advantage that its basic principles are equally well applicable to quite a variety of different systems. As a reflection of this general applicability, the spectrum of analyses, presented in the monograph, includes condensation and boiling, crystallization and melting, self-organization of ferroelectric domains and nanofilms, for-

mation of micellar solutions, formation and growth of diamonds from vitreous carbon. The analysis of different types of phase equilibria and different applications of the nucleation theory starts with a comparison of similarities and differences of solid–liquid and liquid–vapor phase transitions (Chap. 2). It is followed by an extended review of the state of knowledge in the field of nucleation and crystallization kinetics in silicate glasses (Chap. 4) as a particular example of the phase transition liquid–solid. An overview of the kinetics of boiling of binary liquid–gas solutions is given in Chap. 5. In Chap. 6, it is shown that nucleation concepts can be applied successfully to the description of the polarization reversal phenomenon in ferroelectric materials allowing the treatment of different modes of domain evolution from a single universal point of view. Of similar current direct technological significance are the analyses of formation and growth processes of nanofilms on surfaces reviewed in Chap. 7. Chapter 8 deals with an overview on traditional and novel methods of diamond synthesis, while Chap. 9 employs nucleation theory methods to the description of micellization processes. Some summary of the results and outlook on possible future developments is given in Chap. 12.

All of the chapters included in the present book are written by internationally outstanding scientists in their respective fields. It is of particular pleasure to have among the authors the Corresponding Member of the Ukrainian Academy of Sciences, Vitali V. Slezov (Slyozov), one of the authors of the well-known L(ifshitz)S(lezov)W(agner)-theory of coarsening, the description of the late stages of first-order phase transitions being till now one of the corner stones of the theory of first-order phase transformation processes, the Member of the Russian Academy of Sciences, Vladimir P. Skripov, well known for his enormous work devoted, in particular, to the kinetics of boiling processes and reflected in part in his book *Metastable Liquids*, published also by Wiley in 1974 [3], the member of the Russian Academy of Sciences, Anatoli I. Rusanov, well known for his monographs devoted to the thermodynamics of heterogeneous systems which has served as a comprehensive introduction to these topics for decades, and the Member of the Bulgarian Academy of Sciences, Ivan S. Gutzow, who continued with his colleagues and coworkers the traditions of the Bulgarian school of nucleation theory originated by Ivan Stranski and Rostislav A. Kaischew.

As already mentioned in the preface, the contributions, included in the present book, have been presented and discussed in detail at the Research Workshops *Nucleation Theory and Applications* in Dubna, Russia, in the course of the years 1997–2003. Of course, neither all the contributions presented nor all of the results obtained in the common research can be reflected in one book. Some other highly interesting topics are contained in the specialized workshop proceedings [1] and in the publications [2–15] of the participants of the meetings and the authors of the present book we refer to for a more detailed outline of some of the topics discussed here and related aspects.

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2 Solid–Liquid and Liquid–Vapor Phase Transitions: Similarities and Differences

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Every theory, whether in the physical or biological or social sciences, distorts reality in that it oversimplifies. But if it is a good theory, what is omitted is outweighed by the beam of light and understanding thrown over diverse facts.

Paul A. Samuelson

A comparison has been made between the behavior of the thermodynamic properties of simple substances along the curves of solid–liquid and liquid–vapor phase equilibrium. Hereby the attention is concentrated on the internal pressure p_i , the isothermal elasticity $-(\partial p/\partial v)_T$, the surface energy of the interfacial boundary σ , and the viscosity of the liquid, η . The mentioned curves have been extended beyond the triple point into the region of coexistence of metastable phases. Both phase transitions considered approach here the boundaries of stability of the liquid, but in opposite directions from the triple point with respect to variations of temperature and pressure. Among other consequences, the difference in the thermodynamic behavior of one-component systems for both types of phase transformations, as established in the analysis, gives support to the theoretical idea of the absence of a critical point for the solid–liquid phase equilibrium curve.

2.1 Introduction

From a thermodynamic point of view, liquid–vapor (LV) and solid–liquid (SL) first-order phase transitions have much in common. In both cases, the equilibrium of coexisting phases is determined via equality of the chemical potentials, μ , of the coexisting phases. For a solid–liquid equilibrium, we have for example

$$\mu_S(T, p) = \mu_L(T, p). \quad (2.1)$$

The differential form of this equality leads to the Clausius–Clapeyron equation

$$\frac{dp}{dT_{SL}} = \frac{\Delta s_{SL}}{\Delta v_{SL}}, \quad (2.2)$$

where $\Delta s_{SL} = s_L - s_S$, $\Delta v_{SL} = v_L - v_S$ are entropy and volume changes during melting, respectively.

But there are also significant qualitative distinctions between the behavior of the liquid–vapor and solid–liquid equilibrium coexistence curves. One of them consists in the fact that the phase coexistence curve for liquid–vapor equilibrium $p = p_{LV}(T)$ has a lower limit at pressure $p = 0$, whereas the solid–liquid coexistence curve may be extended into the region

of negative pressures, where both coexistent phases are metastable. This extension has, at $T \rightarrow 0$, no universal low pressure limiting value, p_* . Differences in the behavior of liquid–vapor and solid–liquid coexistence curves are also observed for high values of temperature, T , and pressure, p .

A fundamental fact, concerning the properties of liquid–vapor phase equilibria, has been established long ago by Andrews [1]: There exists an upper end point for the equilibrium coexistence of both fluid phases – the critical point. It is characterized by the well-defined values of the parameters T_c , p_c , and v_c , denoted as critical temperature, pressure, and volume. With increasing temperature and pressure (both having initially values lower than T_c and p_c) the properties of the different coexisting phases move closer and become indistinguishable at the critical point itself. This feature of the coexistence curve allows for the possibility of performing a continuous (without change of homogeneity of the substance) liquid–vapor phase transition by choosing a path around the critical point. In such a continuous transition, the trajectory in the space of thermodynamic variables intersects neither the line of phase equilibrium (binodal) nor the region of unstable states, where the elasticity $-(\partial p/\partial v)_T$ is negative. The main difference between the solid–liquid from the liquid–vapor transition consists in the absence of a critical point. This result can be considered as a well-established fact as well [2]. New physical information is permanently accumulated supporting the point of view as outlined above and so far no indications are found requiring for its revision.

The above-mentioned difference of solid–liquid and liquid–vapor phase transitions leads to a number of thermodynamic consequences, which manifest themselves in the thermodynamic behavior of the different systems and, consequently, in the theoretical dependences describing them. One of such generalizations of experimental data for phase coexistence is the Simon equation for the description of the melting line in temperature–pressure variables [3]. It reads

$$1 + \frac{p}{p_*} = \left(\frac{T}{T_0}\right)^c. \quad (2.3)$$

Here $p_* = -p(T \rightarrow 0) > 0$ is an individual parameter which may vary in dependence of the substance considered. Generally it stands for the limiting (for $T \rightarrow 0$) value of pressure (taken with the opposite sign) on the extension of the melting line, T_0 is the temperature at which the melting line intersects the isobar $p = 0$ and c is another individual parameter of the system under consideration.

From the paper of 1929 by Simon and Glatzel [3] one can see that, in processing experimental data, the authors had to discard any possible analogy in the interpretation of experimental results on liquid–solid equilibria as compared with liquid–vapor equilibrium, where the relationship between pressure and temperature is close to a semi-logarithmic one. The power-type dependence, as given by Eq. (2.3), proved to give a satisfactory description. It can further be simplified and generalized by the introduction of a *shifted* pressure scale, p^+ , via

$$p^+ = p + p_*. \quad (2.4)$$

The introduction of the pressure p^+ allows a transformation of Eq. (2.3) into the canonical form

$$\frac{p_1^+}{p_2^+} = \left(\frac{T_1}{T_2}\right)^c, \quad (2.5)$$

not containing any more the individual parameter p_* . It emphasizes the automorphism of the melting lines and the meaning of the individual exponent c as the parameter of thermodynamic similarity of different groups of substances.

Since c is a constant, we can derive the following estimate for its possible values. First, we rewrite Eq. (2.3) in the differential form as

$$\frac{dp}{dT} = p_* \frac{c}{T} \left(\frac{T}{T_0} \right)^{c-1}. \quad (2.6)$$

Further, from the third law of thermodynamics, we have the condition $(dp/dT) \rightarrow 0$ at $T \rightarrow 0$. Consequently, in order to get finite values of c in the whole range of temperatures (including $T \rightarrow 0$), Eq. (2.6) yields the inequality $c > 1$.

Equation (2.3) has not got any additional theoretical substantiation so far similar, e.g., to the van der Waals equation of state for liquid–vapor phase equilibria. Its advantage (and justification) is that it reproduces satisfactorily the relationship between temperature and pressure [4] along the line of phase equilibrium. Another difference to van der Waals' and similar equations of state is that it does not contain the densities of coexisting phases. In his note [5], Simon discussed briefly the relation between Eq. (2.3) and the van der Waals equation, but this direction of research was not developed further by him.

We emphasize that the absence of the critical point of solid–liquid equilibrium makes the solid–liquid different from the liquid–vapor phase transition in the sense that there is no continuous equation of state $f(T, p, v) = 0$ of the type of the van der Waals equation, which would include the description of three states of aggregation. In particular, at $T < T_c$ in the (v, p) plane there is no common isotherm for solid and fluid states (see Fig. 2.1). It is well known that not only the van der Waals equation, but also other existing more sophisticated continuous equations of state do not allow for a combined description of the T , p , and v properties of a fluid and a crystal.

Figure 2.1 represents the following common peculiarity of fluid states. At $T < T_c$, there are two branches of the spinodal. These two curves are determined by the equation

$$\left(\frac{\partial p}{\partial v} \right)_T = 0. \quad (2.7)$$

They merge at the critical point. One of the branches refers to a superheated (stretched) liquid, the other – to a supercooled (supercompressed) gas, but there is no spinodal for supercompressed (supercooled) liquid states [6, 7], i.e., no other extremum exists on the extension BA of each isotherm for high pressures. The point F in Fig. 2.1 specifies the location of the spinodal (for the given value of temperature) of the stretched (superheated) crystal.

If in the (T, p) plane we construct a family of isochores for the liquid and the vapor phases extending them up to the spinodal, we can reveal an exciting feature: each of the branches of the spinodal curve turns out to be the envelope of the corresponding group of isochores [8]. Formally it means that, at any arbitrary point of the spinodal, the condition

$$\left(\frac{dp}{dT} \right)_{s_p} = \left(\frac{\partial p}{\partial T} \right)_v \quad (2.8)$$

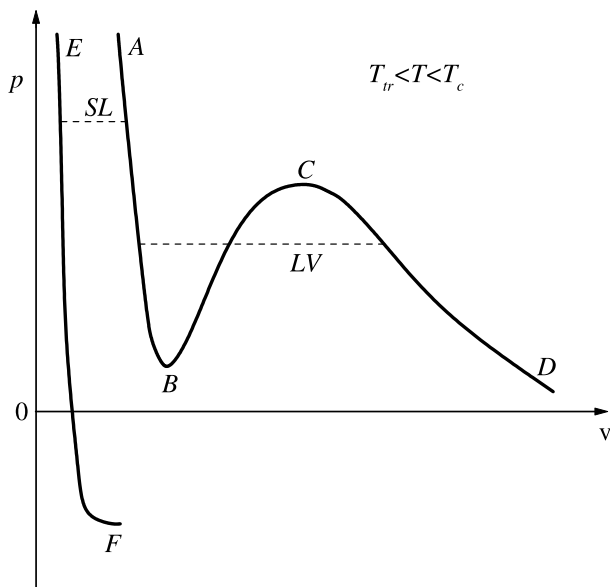


Figure 2.1: Crystalline (EF) and fluid (ABCD) branches of the isotherm in the range $T_{tr} < T < T_c$, where T_{tr} is the temperature of the triple point, T_c the critical point and F, B, and C are the spinodal points on the plane $T = \text{const}$ for solid, liquid, and vapor. The dashed lines (SL) and (LV) correspond to equilibrium phase transitions

is fulfilled. In Fig. 2.2, the results of such a construction are shown for argon [9] employing experimental (T, p, v) data and the extrapolation of the isochores beyond the binodal curve AC.

Employing the van der Waals or similar equations of state for liquid–vapor phase equilibria, the binodal curve can be determined via the Maxwell rule. This method of determination of the points along the binodal curve is not applicable for solid–liquid phase coexistence. In searching for alternative methods of determination of the binodal curves for liquid–solid phase equilibria, one has to guarantee agreement of Eq. (2.3) with the condition $\mu_S(T, p) = \mu_L(T, p)$, and therefore with the Clausius–Clapeyron equation (2.2).

The aim of the present contribution consists in the analysis of the behavior of some basic thermodynamic quantities reflecting the specific character of phase transitions on the solid–liquid and liquid–vapor phase equilibrium lines extended beyond the triple point. Hereby experimental (T, p, v) data are employed for liquids in the stable state and their extrapolation along chosen isolines into the region of metastability. We have restricted ourselves here to the consideration of normally melting substances, for which the relations $dp/dT_{SL} > 0$ and $\Delta v_{SL} > 0$ hold.

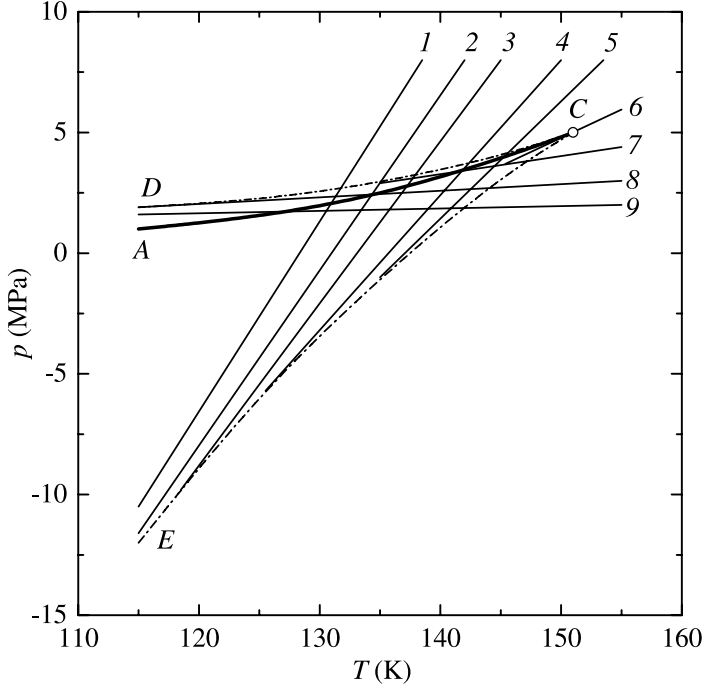


Figure 2.2: Phase diagram of fluid states of argon: AC is the binodal curve, EC is the spinodal of the liquid, DC is the vapor spinodal, (1–5) are a set of liquid phase isochores, (6) is the critical isochore ($v_c = 1.867 \times 10^{-3} \text{m}^3/\text{kg}$), (7–9) are isochores of the vapor

2.2 Behavior of the Internal Pressure

The internal pressure, p_i , of an isotropic phase is determined by the derivative of the internal energy, u , with respect to the volume, i.e.,

$$p_i = \left(\frac{\partial u}{\partial v} \right)_T. \quad (2.9)$$

In a thermodynamic equilibrium state, the internal (p_i) and the external (p) pressures are related by the following equation

$$p_i = T \left(\frac{\partial p}{\partial T} \right)_v - p = p_t - p, \quad (2.10)$$

where

$$p_t = T \left(\frac{\partial p}{\partial T} \right)_v \quad (2.11)$$

is called the thermal or total pressure. The behavior of the internal pressure during changes of the state of the system reflects the variations in the relationship between the forces of attraction

($p_i > 0$) and repulsion ($p_i < 0$) with position averaging over all particles. The values of the pressures p_l and p_i in the different states of the system under consideration can be calculated by Eqs. (2.10) and (2.11), if the thermal equation of state of the substance is known.

With Eq. (2.2) and the relation

$$T \Delta s = \Delta h = \Delta u + p \Delta v , \quad (2.12)$$

where h is the enthalpy, we can introduce another quantity \hat{p} . This quantity has the dimension of pressure as well and is another important characteristic of the phase transition. For the liquid–vapor phase transition, we have then

$$\hat{p}_{LV} \equiv \left(\frac{\Delta u}{\Delta v} \right)_{LV} = T \frac{dp}{dT_{LV}} - p . \quad (2.13)$$

The respective notations for the solid–liquid phase transition may be introduced in a similar way. Equations (2.10) and (2.13) are close to each other in form. However, the specific volumes, v , of the liquid along the liquid–vapor and solid–liquid coexistence curves change differently with increasing temperature: In the first case $dv_L/dT_{LV} > 0$ holds, whereas $dv_L/dT_{SL} < 0$. There is also a difference in the relative slope of the phase transition line on the (T, p) plane and the family of isochores at the points of attachment of isochores to this line: For the solid–liquid line we have

$$\frac{dp}{dT_{SL}} > \left(\frac{\partial p}{\partial T} \right)_v , \quad (2.14)$$

whereas

$$\frac{dp}{dT_{LV}} < \left(\frac{\partial p}{\partial T} \right)_v . \quad (2.15)$$

These results mean that, if we take into account Eqs. (2.10) and (2.13), the quantity \hat{p}_{SL} is larger and \hat{p}_{LV} is smaller than the corresponding internal pressures p_i in the liquid at the lines of phase equilibrium. Including into consideration the low-temperature range of metastable states of the coexisting phases we note that the relations $\hat{p}_{LV}, p_{i,LV} \rightarrow 0$ at $T \rightarrow 0$ hold for liquid–vapor equilibrium, whereas in the same limit $\hat{p}_{SL}, p_{i,SL} \rightarrow p_*$. This result follows from Eqs. (2.10), (2.13), and (2.3). At any arbitrary point of the melting line, we have

$$\hat{p}_{SL} = cp_* + (c - 1)p . \quad (2.16)$$

The lines $p_{i,LV}(T)$ and $p_{i,SL}(T)$, pertaining to the liquid, intersect at the triple point.

Figure 2.3 shows the behavior of the quantities p_{SL} and p_{LV} as well as p_i and \hat{p} for the liquid phase along the lines of the liquid–solid and liquid–vapor equilibrium for argon (a) and sodium (b). To construct the $p_i(T)$ and $\hat{p}(T)$ curves the (T, p, v) data were used from Ref. [10] for argon and Refs. [11, 12] for sodium. Melting lines have been extended into the region $p < 0$ by Eq. (2.3).

From the constructions in Fig. 2.3 it can be seen that the values of \hat{p}_{SL} and $p_{i,SL}$ diverge rapidly with increasing temperature and pressure. This property is connected with the absence

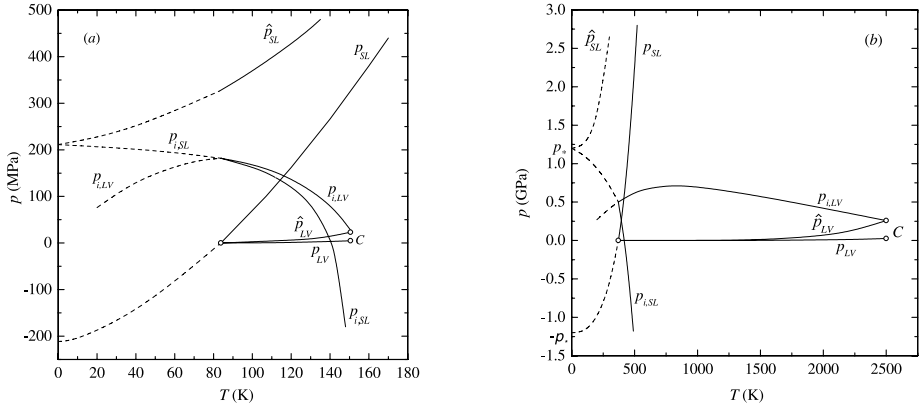


Figure 2.3: Behavior of the internal pressure, p_i , in the liquid and of the quantity, \hat{p} , given by Eq. (2.13), on the lines of solid–liquid ($p_{SL}(T)$) and liquid–vapor ($p_{LV}(T)$) phase equilibrium for argon (a) and sodium (b), C is the critical point. The dashed sections of the curves show the extension beyond the triple point into the region of metastable states

of an end point for solid–liquid equilibrium of critical-point type. The existence of a critical point for liquid–vapor equilibrium leads above the triple point to an approach of the $p_{i,LV}$ and \hat{p}_{LV} lines with increasing temperature and their convergence at the critical point. For solid–liquid equilibrium the values of \hat{p} and p_i coincide only at $T \rightarrow 0$.

On the whole line of liquid–vapor equilibrium the internal pressure is positive, $p_i > \hat{p}_{LV} > 0$, whereas on the melting line the internal pressure passes, with increasing temperature, through zero and becomes negative. Note that, according to the van der Waals equation of state, we have $p_i = a/v^2$, i.e., everywhere $p_i > 0$ holds. This result indicates the inadequacy of the van der Waals equation at high densities of the fluids. In addition, the above considerations also give support to the well-known point of view that a liquid–solid phase transition is not connected with the predominance of attractive forces in the molecular system as is the case in the phenomenon of gas condensation.

2.3 The Boundaries of Stability of a Liquid

The coexistence of two phases presupposes stability of each of them with respect to local perturbations of density or entropy. The condition of mechanical stability

$$-\left(\frac{\partial p}{\partial v}\right)_T > 0 \quad (2.17)$$

has to be fulfilled for each of the phases on the liquid–vapor and solid–liquid coexistence curves including the metastable sections of these lines. Thus, Eq. (2.7) corresponds to the boundary of stability – the spinodal.

It is interesting to reveal the tendency in the relative position of the low-temperature sections of the melting line and the liquid spinodal. For these purposes, a (T, p) diagram